HYDROGEN UTILIZATION DURING THE EARLY
STAGE OF COAL LIQUEFACTION

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In the study of the chemistry of direct coal liquefaction, many of the more interesting aspects concern the initial conversion of coal into products extractable by polar solvents such as tetrahydrofuran. Among these are questions about the type and extent of the various chemical reactions necessary to convert the macromolecular matrix of coal to extractable fragments. The breakdown of the matrix is often depicted as a consequence of thermolysis of cross-linking bonds in coal. However, it is not yet clear to what extent the actions of the solvents, reducing gases, or catalysts applied to the coal are confined to events after the initial thermolytic reactions or to what extent they act directly on the macromolecular matrix itself.

Hydrogen transfer reactions are common to all stages of coal liquefaction. In previous work [1,2], a method was developed and used to determine net hydrogen utilization in the course of liquefaction. The total organic feed and the total organic product were considered in this analysis. The use of hydrogen was divided into four categories according to the type of reaction involved. These include (1) the production of light hydrocarbon gases, (2) removal of heteroatoms, (3) hydrogenation/dehydrogenation reactions involving changes in aromaticity, and (4) the sum of matrix cleavage reactions and condensation reactions. This same method has now been used to determine the changes in the amount of reactions in these four categories during the early stages of coal conversion. A wide variety of conversion conditions was surveyed to explore the sensitivity of hydrogen utilization to important process variables. These variables include the temperature, the reducing gas, the catalyst, and the use of water rather than an organic solvent as the liquefaction medium.

Experimental

Coal liquefaction was conducted in a 0.5-L stirred autoclave. In a typical experiment, 30 to 50 g (maf) of coal ground to pass 60 mesh was charged to the autoclave along with water or coal-derived solvent. When used, the solvent was a distillate cut (240°C-450°C) obtained from operations at the SRC-II pilot plant formerly at Ft. Lewis, Wash. The autoclave was pressurized with the appropriate amount of gas to obtain the desired partial pressure at operating temperature. Heat-up times to liquefaction temperatures were about 45 minutes. The autoclave was held at temperature for the specified time and then rapidly cooled by means of internal water-cooling coils. Grab samples of the off-gas were taken for analysis by gas chromatography as the autoclave was depressurized.

Conversion data were obtained by subjecting the entire autoclave contents to exhaustive Soxhlet extraction with tetrahydrofuran (THF). After extraction, the residues were dried in a vacuum oven at 110°C and weighed. Conversion values were based on the weight of dried residue.

The method used to determine hydrogen utilization data has been described [1]. In brief, the elemental analyses were obtained for the feed coal and the liquefaction solvent. The liquid products were separated into methylene chloride extracts and residues by Soxhlet extraction. Elemental analyses and carbon aromaticities were obtained for both fractions. The carbon aromaticities were

determined by ^{13}C NMR using CP/MAS techniques on the insoluble fractions, and high resolution ^{13}C NMR in CD_2Cl_2 for the extracts. An estimate of the amount of hydrocarbon gas produced was also made on the basis of gas chromatographic analysis of the grab sample of off-gas and the estimate of gas volume based on pressure measurements.

The coal was an Illinois No. 6 bituminous coal from the River King mine. The elemental analysis on an maf basis was as follows: C, 73.7%; H, 5.6%; N, 1.5%; O, 14.8%; and S, 4.5%. The ash content was 13.6% on a dry basis.

Results and Discussion

Dispersed catalysts may be effective in coal conversion at relatively low liquefaction temperatures, especially at low solvent-to-coal ratios. Figure 1 contains conversion data as a function of solvent-to-coal ratio obtained after holding the temperature at 350°C for 60 minutes under 2000 psia hydrogen. As reflected by tetrahydrofuran conversion values, the effect of adding ammonium molybdate (1% molybdenum on maf coal weight) becomes pronounced at low solvent/coal ratios. In this sense, use of catalyst under H_2 pressure reduces the demand for the large quantities of recycle solvent normally required for good conversion in the absence of catalyst. High conversions may thus be obtained at low solvent/coal ratios. Regarding the mechanism of liquefaction, these data indicate that catalysts can play a role in the breakdown of the coal matrix that leads to the initial formation of extractable products.

Table 1 compares the effects of liquefaction temperature on hydrogen utilization at the more conventional solvent/coal ratio of 2. The two catalysts used, ammonium molybdate and tin tetrachloride, were thought to act in liquefaction by different means [3]. The former is noted for hydrogenation activity, and the latter is not. However, differences in the hydrogen utilization data between the two were not striking.

As determined earlier [1,2], temperature has a large effect on the pattern of utilization. There is a change from net hydrogenation to net dehydrogenation between 375°C and 425°C. The net change at 400°C was zero. Hydrogen partial pressure at temperature was roughly the same, 2000 psia, in all cases. The direction of the change from net hydrogenation to net dehydrogenation is expected from thermodynamic considerations. At equilibrium, higher temperatures generally favor the formation of aromatic compounds from hydroaromatic compounds by release of hydrogen. These data emphasize the important effect of temperature and the degree of control possible within a short span of temperature centered around 400°C.

The addition of the catalysts at 425°C had a large effect on the amount of hydrogen consumed during the cleavage of matrix bonds. The method measures net hydrogen utilization without regard to the details of the chemical mechanism. Thus, from these data alone it cannot be said whether the increase in hydrogen use is due to promotion of bond cleavage directly or to the prevention of condensation reactions between reactive fragments created by simple thermal bond scission. At 375°C, there was little net change in matrix bonds in the presence of ammonium molybdate and no net change in the absence of catalyst. Of course, since only net changes are measured, this does not necessarily mean that matrix bond cleavage did not occur. It may be that cleavage reactions are nearly balanced by condensation reactions.

The amount of hydrogen consumed to remove heteroatoms is relatively small, as expected under mild liquefaction conditions. Almost all of this hydrogen is used in the removal of oxygen. There is essentially no change in nitrogen content and only a small reduction of organic sulfur.

In a separate series of autoclave experiments, liquefaction with water was compared to that with the organic liquefaction solvent. In some respects, interpretation of the data obtained with water was simplified because now all of the organic liquefaction products originate from the coal. However, coal may behave quite differently in water than in organic solvents. In particular, conversions in water vary greatly depending on the type and partial pressure of the reducing gas and on the type of catalyst used.

Table II contains liquefaction data obtained at 350°C. At this mild temperature, conversions are very low using water as a solvent under hydrogen. By comparison, conversions were much higher even at a shorter contact time using SRC-II distillate. They were also less sensitive to hydrogen partial pressure in the hydrocarbon solvent.

When coal was recovered from the experiments with water and hydrogen at room temperature partial pressures less than 1500 psia, it appeared not to have agglomerated nor to have lost its particulate nature. Sufficient conversion to cause agglomeration did occur under 2000 psia hydrogen partial pressure. In contrast, under only 1000 psia room temperature partial pressure of CO, the coal was generally recovered as an agglomerated mass. Conversions were much higher under CO than under hydrogen at the same pressure and were improved further by use of ammonium molybdate and even more so by basic catalysts, K_2S in particular. Clearly, the mechanisms of liquefaction must be quite different according to whether CO or H_2 is used as the reducing gas. These findings are similar to those of an earlier comparison of hydrogen and carbon monoxide used with water in the presence or absence of base [4].

Hydrogen utilization data were obtained for a variety of reaction conditions with water (Table III). Many of these hydrogen utilization values are larger than those in Table I. If the speculation that coal accounts for the majority of the reactions using hydrogen when organic solvent is present is accepted, then the increase in the absolute magnitude of the utilization values is easily understood. The organic solvent may act as a diluent that reduces the observed amount of hydrogen used or given up per 100 carbons of the total feed. In water, however, all of the carbon is associated with the coal, thus resulting in observation of larger changes. Aside from this dilution factor, there seems to be a general trend for coal to give up hydrogen more readily by dehydrogenation and condensation reactions in water than does the total mixed feed of coal and recycle solvent.

In water, temperature is again a major determinant of the pattern of hydrogen utilization. At 400°C there is an overall net loss of hydrogen by coal. Generally, the loss is split between dehydrogenation reactions and condensation reactions. The latter are reflected as negative values for matrix cleavage. In contrast, at 350°C under CO, there is little change in total hydrogen in the absence of catalyst. In the presence of KOH, there is a sizable uptake of hydrogen.

The type of reducing gas has a large influence at 350°C. With either H_2 or N_2 replacing CO, there is again a large net loss of hydrogen by coal. The loss is accounted for by both dehydrogenation and condensation, as it was at 400°C.

Other general trends are also apparent. Gas make is virtually nil at 350°C. The loss of heteroatoms, which is almost totally due to loss of oxygen in these experiments, is not as great at 350°C as at 400°C. The exception to this observation is the higher value at 350°C for the one experiment run for 120 minutes. Thus, the rate of loss may be slower at the lower temperature.

The role of catalyst is also closely related to liquefaction temperature. Although the data are incomplete, addition of KOH markedly increases the total amount of hydrogen taken up by coal at 350°C. At 400°C, the difference on addition

of KOH is mostly associated with an increased loss of hydrogen by condensation reactions.

The reaction conditions surveyed here indicate that hydrogen utilization varies considerably with liquefaction conditions. Temperature, reducing gas, and catalyst were major influences. These data provide added confidence that the analytical method reveals real changes in liquefaction mechanisms. A full picture of hydrogen utilization requires a much more extensive comparison among the myriad of process parameters. Further studies now under way are aimed at identifying other critical parameters, such as reaction time.

References

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Acknowledgements

Table I. Coal Conversion and Hydrogen Utilization for
Catalyzed and Non-Catalyzed Liquefaction[1]

Catalyst	Temperature	Heteroatom Removal	Hydrogenation	Matrix Cleavage	Gas Make	Total[2]
Ammonium Molybdate	375°C	1	2	2	0	5
SnCl₄	375°C	0	4	0	0	4
Ammonium Molybdate	400°C	2	0	2	0	4
None	425°C	2	-5	5	1	3
Ammonium Molybdate	425°C	2	-4	11	2	11
SnCl₄	425°C	1	-4	10	2	9

[1]All liquefactions under approximately 2000 psia hydrogen partial pressure at operating temperature, using 2 parts solvent and 1 part maf coal.

[2]All utilization numbers in hydrogens per 100 carbons in feed slurry.

TABLE II. Coal Conversion at 350°C

Solvent[1]	Gas, psia[2]	Time, min.	Catalyst[3]	Conversion[4]
SRC-II	H_2, 200	15		66
SRC-II	H_2, 1000	15		68
SRC-II	H_2, 2000	15		75
SRC-II	H_2, 3000	15		80
Water	H_2, 1100	60		16
Water	N_2, 1010	60		12
Water	H_2, 1100	60	AmMo (0.2%)	19
Water	H_2, 1500	60		33
Water	H_2, 2000	60		57
Water	CO, 1000	60		63
Water	CO, 1010	60	K_2S (2%)	93
Water	CO, 1010	60	AmMo (0.2%)	71
Water	CO, 1020	60	AmMo (0.4%)	82
Water	CO, 1000	60	KOH (1%), AmMo (0.4%)	86

[1]Two parts solvent used to one part coal, by weight.

[2]With SRC-II, pressure is measured at operating temperature. With water, pressure is measured at room temperature.

[3]Catalyst loading is weight percent on maf coal. For ammonium molybdate, AmMo , based on weight of molybdenum.

[4]Based on residue weights after exhaustive Soxhlet extraction with tetrahydrofuran.

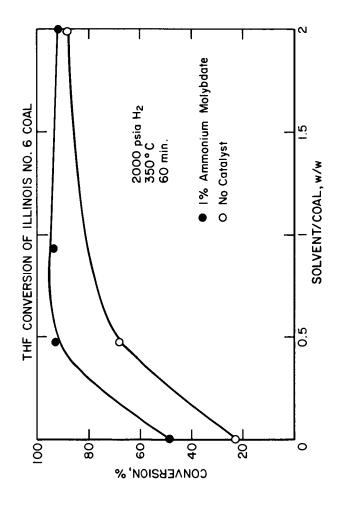Table III. Hydrogen Utilization for Liquefaction in Water

Temperature	Catalyst[1]	Pressure[2], psia	Time, min.	Heteroatom Removal	Hydrogenation	Matrix Cleavage	Gas Make	Total[3]
400°C		750	15	4	-9	-2	2	-5
400°C		800 (H_2)	20	3	-11	-5	1	-12
400°C	KOH	800	20	6	-7	-7	2	-6
400°C	KOH	800	60	7	-6	-5	2	-2
400°C	Na^+HCOO^-	730	20	6	-12	-5	2	-9
350°C		1000	120	5	-1	-1	0	2
350°C		1000	60	3	-2	0	0	1
350°C	KOH	1000	60	3	NA	NA	0	9
350°C	AmMo	1000	60	3	-1	-1	0	1
350°C		1000 (H_2)	60	2	-5	-8	0	-11
350°C		1000 (N_2)	60	4	-7	-7	0	-10

[1]Catalyst loadings were 1% by weight of KOH or sodium formate, or 0.4% of ammonium molybdate, AmMo.

[2]Pressure measured at room temperature. Reducing gas used is CO unless otherwise indicated.

[3]Hydrogen utilization in hydrogens per 100 carbons in coal.

THF CONVERSION OF ILLINOIS NO. 6 COAL

2000 psia H₂
350°C
60 min.

● 1% Ammonium Molybdate
○ No Catalyst

SOLVENT/COAL, w/w

CONVERSION, %

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